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(54) Ink jet recording paper and labels made therefrom.

(57) An ink jet recording paper comprises a substrate which is coated with at least 0.1 g/m^2 or borax or boric acid on at least one side, and an ink jet recording layer formed on one borax or boric acid-coated side, at a coverage of 5-20 g/m^2. The recording layer comprises 100 parts by weight of a pigment having a synthetic silica as its main ingredient and 10-35 parts by weight of a binder having polyvinyl alcohol as its main ingredient. Both improved scratch strength and high resolution are thereby achieved. An ink jet recording label incorporating said recording paper is also described.

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This invention relates to an ink jet recording paper having a high scratch strength recording layer and ink jet recording labels made therefrom.

There are various mechanisms by which ink jet recording may be accomplished. In all of these mechanisms, however, recording is effected by ejecting fine ink droplets, and making these droplets adhere to recording paper so as to form dots. Compared to dot impact recording techniques, ink jet recording offers the advantages of noiselessness, easy adaptation to full colour recording, and the possibility of high speed printing.

Recently, in response to many different types of demand and a greater need for better classification, a wider application is emerging for labels consisting of paper recorded by ink jet which can be affixed to a variety of different goods.

In such applications, an ink jet recording paper wherein the recording layer has high scratch strength is required from the viewpoint of durability. Further, in label applications, it is required in many cases that high resolution printing can be performed so that characters can be recorded, and in particular so that small characters are sufficiently clear and distinct. Conventional coat-type ink jet recording paper however suffers from the disadvantages that its frictional resistance and scratch resistance are inadequate, and that in some cases small characters cannot be distinguished. For these reasons, it is unable to satisfy the aforesaid requirements.

If, in order to improve the scratch strength of the ink jet recording layer, the amount of binder in the layer is merely increased, printed dots spread out and fine lines become thicker, so that the desired recording properties are not obtained. In other words, from the viewpoint of obtaining high resolution it is desirable to reduce the amount of binder, and this is contrary to the purpose of increasing the scratch strength of the recording layer.

To achieve the dual objectives of improving the scratch strength of the recording layer and obtaining high resolution, the inventors of the present invention carried out various studies on ink jet recording paper. As a result of these studies, it has been found that satisfactory results can be achieved by treating the paper with both borax or boric acid and polyvinyl alcohol.

It is therefore a primary object of this invention to provide a coat-type ink jet recording paper in which the recording layer has high scratch strength, and also allows high resolution to be achieved.

It is a further object of this invention to provide a coat-type label for ink jet recording which affords high resolution, and in which the recording layer has sufficient scratch strength.

The above objects of the invention are attained by an ink jet recording paper comprising a substrate which is coated with at least 0.1 g/m^2 of borax or boric acid on at least one side, and an ink jet recording layer which is coated at a coverage of 5-20 g/m^2 on one coated surface of the substrate, with the ink jet recording layer comprising 100 parts by weight of a pigment having a synthetic silica as its main ingredient and 10 - 35 parts by weight of a binder having polyvinyl alcohol as its main ingredient; and by an ink jet recording label made from the aforesaid paper.

The layer of borax or boric acid forming an undercoat to the ink jet recording layer, causes gelation of the polyvinyl alcohol in the ink jet recording layer during the coating process, thereby increasing the surface retention of binder and improving the scratch strength of the ink jet recording layer without an increase in the amount of binder. Further, the borax or boric acid and polyvinyl alcohol undergo a crosslinking reaction, so that even when the amount of binder is decreased to a level at which there does not occur such blotting of dots or thickening of fine lines as to impair recording properties, and at which high resolution recording can therefore be performed, sufficient scratch strength of the ink jet recording layer is still maintained.

In the ink jet recording paper and label of the present invention, therefore, the recording layer has high scratch strength and, what is more, has recording resolution high enough to make small characters clear and distinct, or to render them distinguishable.

Some embodiments of the present invention will now be described with reference to the accompany drawings, in which

Fig. 1 is a sectional view illustrating an ink jet recording paper according to the invention;

Fig. 2 is a sectional view illustrating an ink jet recording label according to the invention; and

Fig. 3 is a sectional view illustrating an arrangement in which an ink jet recording label according to the invention is affixed to an object.

In Fig. 1 reference numeral 1 indicates an ink jet recording layer, 2 a borax or boric acid treated layer, and 3 a support.

The support used in this invention may be suitably chosen from any of the materials known in the art, but chemical pulp paper, mechanical woodpulp paper and recycl d paper are particularly to be preferred.

For manufacturing the ink jet recording paper of the present invention, a borax or boric acid treatment is first applied to at least one side of the substrate 3 by coating at least on side of the substrate 3 with an aqueous solution of borax or boric acid. The coating method may be suitably chosen from any of the methods known to those skilled in the art such as the use of an air knife, roller, bar, gravure or size press. The coverage of the

solution on the or each face of the substrate should be at least 0.1 g/m² on a solids basis, but more preferably from 0.2 g/m² to 5 g/m² for borax and more preferably from 0.4 g/m² to 5 g/m² for boric acid.

The ink jet recording layer 1 which is formed on this borax or boric acid layer 2 comprises a pigment having a synthetic silica as its main ingredient and a binder having polyvinyl alcohol as its main ingredient, but it may also contain various auxiliary agents in common use such as dispersants, antifoamers, dyes, fluidity modifiers and the like.

The provision of a borax or boric acid treated layer 2 as described herinbefore causes gelation of the polyvinyl alcohol in the ink jet recording layer 1 during the coating process so that it cannot easily penetrate the paper and increases the surface retention of binder. The scratch strength of the ink jet recording layer 1 can therefore be increased without increasing the amount of binder. Further, the borax or boric acid and polyvinyl alcohol undergo a crosslinking reaction so that scratch strength is maintained even when the amount of binder is reduced.

According to the present invention, the synthetic silica which is the main ingredient of the pigment, that is which constitutes from 60 wt% to 100 wt% of the total amount of pigment, may be suitably chosen from any kind of synthetic silica known in the art, but silica with a large specific surface is particularly to be preferred. Typical examples of such silica are fine silica obtained by the wet process, white carbon, silica gel, and ultrafine silica obtained by the dry process.

The pigment which can be used as an auxiliary ingredient together with the synthetic silica which is the main ingredient, may be suitably chosen from among those known in the art such as kaolin, calcium carbonate, aluminium hydroxide, satin white and aluminium silicate.

According to this invention, the binder of which the main ingredient is polyvinyl alcohol is used in a proportion of 10 - 35 parts by weight with respect to 100 parts by weight of pigment. In this case, a high molecular compound suitably chosen from resins known in the art such as casein, starch, carboxymethyl cellulose, styrene/butadiene latex, acrylic emulsions and vinyl acetate emulsions may be added either as an auxiliary ingredient of the binder or in addition to the aforesaid binder.

The amount of such added auxiliary agent is preferably no greater than 15 parts by weight, and more preferably no greater than 5 parts by weight, of binder.

Further, cationic polyelectrolytes may be added to the ink jet recording layer 1 in order to improve the water resistance of the printed part of the paper.

In general, aqueous ink is used in ink jet recording, so the recording tended to blot or run after printing due to adhesion of water. Cationic polyelectrolytes react with groups such as $-SO_3Na$, $-SO_3H$ and $-NH_2$ in water-soluble direct dye or water-soluble acidic dye molecules in the ink so as to form salts which are insoluble in water, and their addition therefore improves the water resistance of the printed part of the paper. Examples of such cationic polyelectrolytes are polyvinylbenzyltrimethylammonium halides, polydiacryldimethylammonium halides, polydimethyl-aminoethylmethacrylate hydrochloride, polyethyleneimine, dicyanodiamide-formaldehyde condensates, epichlorohydrin-modified polyalkylamines, polyvinylpyridinium halides, and other quaternary ammonium salts and polyamines.

These cationic polyelectrolytes are added in a proportion of 2 parts - 30 parts by weight, and more preferably 4 parts - 20 parts by weight, to 100 parts by weight of pigment, but this proportion may be suitably adjusted depending on the amount of coating material, and the type and quantity of ink to be used.

For coating the recording layer of this invention, any suitable coating means may be used which is known in the art for general manufacture of pigment-coated paper such as a blade coater, air knife coater, roller coater, curtain coater, bar coater, gravure coater or comma coater. The amount of coated material should normally be 5 - 20 g/m², and more preferably 7 - 15 g/m², in terms of solids equivalent for each surface of the paper, but this amount may be adjusted as desired provided that the surface is covered and sufficient ink absorption is obtained.

Fig. 2 is a sectional view of an ink jet recording label comprising a layer of pressure sensitive adhesive 4 covered by a release paper 5 and formed on a support 3 of the recording paper of Fig. 1.

The pressure sensitive adhesive used in the pressure sensitive layer 4 may be either solvent-based or water-based. The pressure sensitive layer 4 and release layer 5 may be fixed on the support by, for example, so-called "transfer coating" wherein a pressure sensitive adhesive is coated onto a release paper or film which has been peel-off treated with a silicone resin or the like, dried, and then laminated with a substrate.

The ink jet recording label of the invention is used by recording on the ink jet recording layer 1, removing the release paper 5, and affixing the label to an object 6 as shown in Fig. 3.

The invention will now be described in more detail with reference to specific Exampl s, but it will be understood that the invention is not to be interpreted as being limited by these Examples in any way.

EXAMPLE 1

A 1 wt% aqueous solution of borax was coated by a size press onto both sides of ordinary woodfree paper with a basis weight of 64 g/m² so as to have a total coverage of 0.4 g/m² (0.2 g/m² on each side) on a solids basis. Further, 100 parts by weight of a synthetic silica (commercial name Finesil X-37: Tokuyama Soda K.K.) was dispersed in 350 parts by weight of water, and mixed with a solution prepared by dissolving 30 parts by weight of polyvinyl alcohol (PVA 117: Kuraray K.K.) in 270 parts by weight of water to give an ink jet recording layer coating colour. This colour was applied with a bar coater to the aforesaid borax-treated paper at a coverage of 15 g/m² on a solids basis, and dried to give an ink jet recording paper.

A recording was made on this ink jet recording paper using an ink jet printer (Epson HG-2500), and the pencil hardness of the coated layer was measured by the JIS K- 5400 pencil scratch test using only H hardness pencils. After the measurement, the scratched surface was subjectively evaluated by visual or tactile means, and the results of the evaluation displayed by the mark ○ or X.

The results are shown in Table 1.

EXAMPLE 2

A 5 wt% aqueous solution of boric acid was coated by a size press onto both sides of ordinary woodfree paper with a basis weight of 75 g/m² so as to have a total coverage of 1.0 g/m² (0.5 g/m² on each side) on a solids basis. The ink jet recording layer coating color used in Example 1 was applied by a bar coater at a coverage of 10 g/m² on a solids basis, and dried to give an ink jet recording paper. This ink jet recording paper was evaluated in the same way as in Example 1, and the results are shown in Table 1.

EXAMPLE 3

100 parts by weight of a synthetic silica (Finesil X-37) was dispersed in 350 parts by weight of water, and mixed with a solution prepared by dissolving 20 parts by weight of polyvinyl alcohol (PVA 117) in 180 parts by weight of water followed by 5 parts by weight of a polyvinylbenzyltrimethylammonium halide to give an ink jet recording layer coating color. This color was applied by a bar coater to the borax-treated paper used in Example 1 at a coverage of 14 g/m² on a solids basis, and dried to give an ink jet recording paper.

The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1. Further, when the recording paper was immersed in water after printing and the paper observed after 5 minutes, there was found to be little running of ink.

EXAMPLE 4

An acrylic emulsion pressure sensitive adhesive (Toughtac 601: Sanyo Kokusaku Pulp K.K.) was coated at a coverage of 20 g/m² on a release paper (EK 120D2: Lintec K. K.). This coated release paper was laminated with the ink jet recording paper obtained in Example 3 to fabricate a label. The ink jet recording label thus obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1. Further, after printing, this label was affixed to a video cassette, and exhibited satisfactory affixing properties without peeling off.

EXAMPLE 5

A 1 wt% aqueous solution of borax was coated by a bar coater onto both sides of ordinary woodfree paper with a basis weight of 64 g/m² so as to have a total coverage of 0.6 g/m² (0.3 g/m² on each side) on a solid basis. Further, 100 parts by weight of a synthetic silica (commercial name Syloid 620: Fuji Davison Chemical Ltd.) was dispersed in 350 parts by weight of water, and mixed with a solution prepared by dissolving 10 parts by weight of polyvinyl alcohol (PVA 117: Kuraray K.K.) in 90 parts by weight of water to give an ink jet recording layer coating color. This color was applied with an air-knife coater to the aforesaid borax-treated paper at a coverage of 20 g/m² on a solids basis, and dried to give an ink jet recording paper. This ink jet recording paper was evaluated in the same way as in Example 1, and the results are shown in Table 1.

EXAMPLE 6

A 1 wt% aqueous solution of boric acid was coated by a bar coater onto both sides of ordinary woodfree paper with a basis weight of 64 g/m² so as to have a total coverage of 0.4 g/m² (0.2 g/m² on each side) on a solids basis. The ink jet recording layer coating color used in Example 5 was applied by an air-knife coater at

a coverage of 5 g/m^2 on a solids basis, and dried to give an ink jet recording paper. This ink jet recording paper was evaluated in the same way as in Example 1, and the results are shown in Table 1.

EXAMPLE 7

A 5 wt% aqueous solution of boric acid was coated by a size press onto both sides of ordinary woodfree paper with a basis weight of 64 g/m^2 so as to have a total coverage of 1.2 g/m^2 (0.6 g/m^2 on each side) on a solids basis. The ink jet recording layer coating color used in Example 5 was applied by a bar coater at a coverage of 18 g/m^2 on a solids basis, and dried to give an ink jet recording paper. This ink jet recording paper was evaluated in the same way as in Example 1, and the results are shown in Table 1.

EXAMPLE 8

A 5 wt% aqueous solution of boric acid was coated by a size press onto both sides of ordinary woodfree paper with a basis weight of 64 g/m^2 so as to have a total coverage of 1.2 g/m^2 (0.6 g/m^2 on each side) on a solids basis. The ink jet recording layer coating color used in Example 5 was applied by a bar coater at a coverage of 5 g/m^2 on a solids basis, and dried to give an ink jet recording paper. This ink jet recording paper was evaluated in the same way as in Example 1, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The ink jet recording layer coating color used in Example 1 was applied to ordinary woodfree paper with a basis weight of 64 g/m^2 so as to have a coverage of 10 g/m^2 on a solids basis, and dried to give an ink jet recording paper. The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1. Further, when the recording paper was immersed in water after printing and the paper observed after 5 minutes, there was found to be some running of the print.

COMPARATIVE EXAMPLE 2

100 parts by weight of a synthetic silica (Finesil X-37) was dispersed in 350 parts by weight of water, and mixed with a solution prepared by dissolving 5 parts by weight of polyvinyl alcohol (PVA 117) in 45 parts by weight of water to give an ink jet recording layer coating color. This color was applied by a bar coater to the borax-treated paper used in Example 1 so as to have a coverage of 14 g/m^2 on a solids basis, and dried to give an ink jet recording paper. The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 3

100 parts by weight of a synthetic silica (Finesil X-37) was dispersed in 350 parts by weight of water, and mixed with a solution prepared by dissolving 50 parts by weight of polyvinyl alcohol (PVA 117) in 450 parts by weight of water to give an ink jet recording layer coating color. This color was applied by a bar coater to the borax-treated paper used in Example 1 so as to have a coverage of 14 g/m^2 on a solids basis, and dried to give an ink jet recording paper. The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 4

The ink jet recording layer coating color used in Example 1 was applied by a bar coater to the borax- treated paper used in Example 2 so as to have a coverage of 2 g/m^2 on a solids basis, and dried to give an ink jet recording paper. The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 5

The ink jet recording layer coating color used in Example 1 was applied by a bar coater to the borax- treated paper used in Example 2 so as to have a coverage of 25 g/m^2 on a solids basis, and dried to give an ink jet recording paper. The recording paper obtained was evaluated in a similar way to Example 1, and the results are shown in Table 1.

TABLE 1

	Coverage of borax (*1)	Coverage of boric acid (*1)	Fraction of PVA (pts.wt.)	Coverage of recording layer (g / m ²)	Quality of dots (*2)	Strength of coated layers (*3)
EXAMPLE 1	0.2	0	30	15	○	○
EXAMPLE 2	0	0.5	30	10	○	○
EXAMPLE 3	0.2	0	20	14	○	○
EXAMPLE 4	0.2	0	20	14	○	○
EXAMPLE 5	0.3	0	10	20	○	○
EXAMPLE 6	0.2	0	10	5	○	○
EXAMPLE 7	0	0.6	10	18	○	○
EXAMPLE 8	0	0.6	10	5	○	○
COMPARATIVE EXAMPLE 1	0	0	30	10	○	×
COMPARATIVE EXAMPLE 2	0.2	0	5	14	○	×
COMPARATIVE EXAMPLE 3	0.2	0	50	14	×	○
COMPARATIVE EXAMPLE 4	0	0.5	30	2	○	△
COMPARATIVE EXAMPLE 5	0	0.5	30	25	×	○

*1 : Per side (g / m ²)

*2 : ○ ; good, and high in sharpness.
× ; inferior in sharpness, including the spread of each dot.

*3 : ○ ; no damage
△ ; slight damage
× ; heavy damage

Claims

1. An ink jet recording paper comprising a substrate and an ink jet recording layer formed thereon, characterised in that the substrate is coated with at least 0.1 g/m^2 of borax or boric acid on at least one face thereof, and in that the ink jet recording layer is formed on the or one of the coated faces of the substrate at a coverage of 5-20 g/m^2 and comprises 100 parts by weight of a pigment having a synthetic silica as the main ingredient and 10-35 parts by weight of a binder having polyvinyl alcohol as the main ingredient.

2. A recording paper as claimed in claim 1, wherein borax is coated on one or both faces of the substrate at a coverage of at least 0.2 g/m^2 per face.

3. A recording paper as claimed in claim 1, wherein boric acid is coated on one or both faces of the substrate at a coverage of at least 0.4 g/m^2 per face.

4. A recording paper as claimed in claim 1, 2 or 3, wherein the amount of synthetic silica is at least 60 wt% of the total amount of pigment.

5. A recording paper as claimed in any preceding claim, wherein the amount of polyvinyl alcohol is at least 85 wt% of the total amount of binder.

6. A recording paper as claimed in any preceding claim, wherein said recording layer additionally contains cationic polyelectrolyte in an amount of 2-30 parts by weight per 100 parts by weight of the pigment.

7. A recording paper as claimed in claim 6, wherein the cationic polyelectrolyte comprises at least one quaternary ammonium salt or polyamine selected from polyvinylbenzyltrimethylammonium halides, polydiacryldimethylammonium halides, polyvinylpyridinium halides, polydimethylaminoethylmethacrylate hydrochloride, polyethyleneimine, dicyanodiamide-formaldehyde condensates and epichlorohydrin-modified polyalkylamines.

8. A recording paper as claimed in any preceding claim, wherein the coated weight of the recording layer is 7-15 g/m^2.

9. An ink jet recording label comprising a paper as claimed in any preceding claim, and a layer of a pressure sensitive adhesive coated on the face of the substrate remote from the recording layer and having a release layer provided thereon.

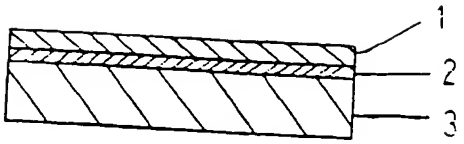

Fig. 1.

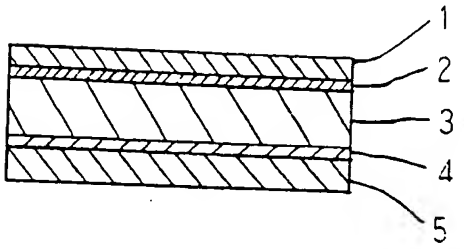

Fig. 2.

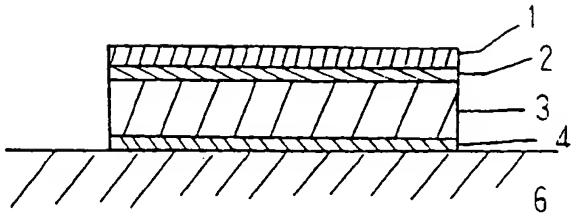

Fig. 3.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1999

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 246 987 (AUSSEDAT-REY) * claims 1-5 *	1-5	B41M5/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 MARCH 1992	FOUQUIER J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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